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PROPERTIES OF MAGNESIUM BASED CEMENTS

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SUMMARY

Mixture of magnesium oxide with either silica fume or phosphate were prepared in this research. The workability, mechanical properties and the microstructure of the two magnesium based binder were examined. Compressive strength tests showed that the magnesium phosphate cement (MPC) gained early strength much faster than magnesium silica hydrate cement (MSH) but the MSH system showed continued long term strength gain. The results from XRD testing confirm that $MgKPO_4 \cdot 6H_2O$ was the main hydration products of MPC and for magnesium silica system there was a considerable amount of brucite which co-existed with MSH. Scanning Electronical Microscopy was used to examine the microstructure and nature of the hydration for both Mg based cements.

INTRODUCTION

Research on magnesium based binder systems as an alternative to Portland cement (PC) has increased significantly in the last decade(Deng 2003, Harrison 2008, Li, Qiao et al. 2010, Nied, Enemark-Rasmussen et al. 2016). The magnesium based cements have potential environmental benefits due to the low calcination temperature coupled with the incorporation of industrial by-products and their potential suitability for heavy-metal-containing waste encapsulation (Wei, Chen et al. 2006, Walling and Provis 2016, Zhang et al. 2011, 2012).

Table 1 summarizes the different types of the major MgO-based cements. Magnesium phosphate cement (MPC) is derived from reactions between phosphate and dead burnt (above 1400 ^oC) magnesium oxide, and can be used as a rapid repair material due to its quick setting, good bonding properties with old concrete and high early strength (Li, Qiao et al. 2010, Li and Chen 2013, Yang, Shi et al. 2014). Magnesium silicate hydrate cement (MSH) are produced from the reaction between magnesium oxide and a source of highly reactive silica(Zhang, Cheeseman et al. 2011, Chiang, Ferraro et al. 2014, Nied, Enemark-Rasmussen et al. 2016). To date there have been no reported commercial application of MSH cement and only limited studies on its mechanical properties or long term durability. However, the moderate pH of MSH binders and its particular hydration reaction indicate it should be ideal immobilizing agent for the disposal of heavy metal wastes.

Table 1. Different types of MgO-based cements

	Magnesium Oxy-Chloride Cement	Magnesium Oxy-Sulfate Cement	Magnesium Phosphate Cement	Magnesium Silica Cement
Raw Materials	$MgO+MgCl_2$	$MgO+MgSO_4$	$MgO+NH_4H_2PO_4$/ KH_2PO_4	$MgO+SiO_2$
Cementitious compounds	$3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$, $5Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$.	$3Mg(OH)_2 \cdot 3MgSO_4 \cdot 8H_2O$, $5Mg(OH)_2 \cdot MgSO_4 \cdot 2H_2O$.	$NH_4MgPO_4 \cdot 6H_2O$/ $KMgPO_4 \cdot 6H_2O$	$Mg(OH)_2$, $3MgO \cdot 2SiO_2 \cdot 2H_2O$
Advantages and limitations	Favorable fire and abrasion resistance, Low thermal conductivity. Poor water stability		Quick setting and high early strength, Good bonding. Poor water resistance	High temperature resistance, low pH and good surface gloss

The present study examines the mechanical properties and microstructure of both Magneisum Phosphate Cement (MPC) and Magnesium Silicate Hydrate (MSH) binder systems prepared at low w/c and various curing conditions. This experimental work is aimed at providing a greater understanding of the potential applications of magnesium based binders as construction materials.

MATERIALS AND METHODS

Materials

Magnesium oxide can be obtained from several sources including through the calcination of magnesium carbonate. Depending on the calcination temperature, the magnesia can be classified into several grades. It can be seen from Table 2 that with increasing calcination temperature, the reactivity decreases. It can be attributed to the reduction of the specific surface area and the increase of the particle size. The magnesia produced above the fusion point is perfectly reorganized and chemically stable.

Among the various types of magnesia, the light burned magnesia, i.e. the reactive magnesia, is the main raw material for the Magnesia Silicate Hydrate (MSH) binder system and the dead burned magnesia is the reaction precursor for the magnesium phosphate system.

Table 2. Different Grades of MgO Based on Calcination Temperature.

Grades	Light Burned	Hard burned	Dead burned	Fused
Calcination temperature	700ºC – 1000ºC	1000ºC – 1500ºC	1500ºC – 2000ºC	Above 2800ºC
Reactivity	High reactivity	Low reactivity	Lower reactivity	Very little reactivity
Applications	Agricultural, catalysts.	Abrasives, building products, ceramics.	Refractory applications.	Refractory and electrical insulating.

In the present investigation, reactive magnesium oxide grade 150 (M) was supplied by Calix Ltd. (Australia). Condensed silica fume (SIKAFUME) was provided by Sika NZ. The condensed silica fume is composed of agglomerates of individual silica fume particles with a size of approximately d_{50} = 0.1 - 0.2µm, determined by SEM analysis. Mono-potassium phosphate is

a water soluble crystal with a particle size around 245~350um. River sand was locally sourced and sieved to provide a maximum aggregate size of 2.36mm (FM=1.9). A third generation polymer-based superplasticizer (SP) (Viscocrete-5-555) provided by Sika NZ was selected to provide adequate workability. The particle size distributions of the binder constituents determined by SEM, Laser diffraction, and sieve method are presented in Figure 1. The oxide composition of the binder components are provided in Table 3.

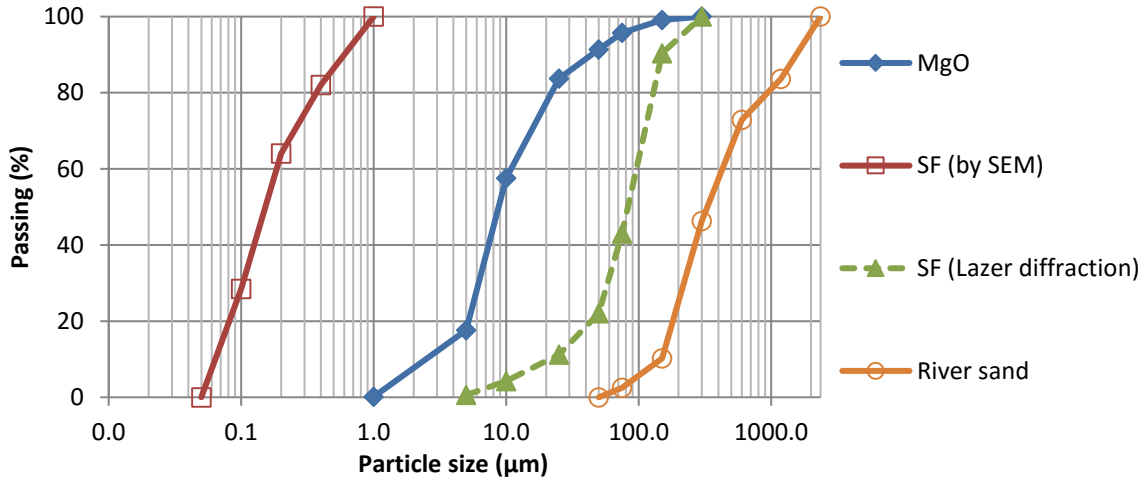


Figure 1. Particle size distribution of raw materials

Table 3. Chemical composition of raw materials

Sample	SiO_2 (%)	TiO_2 (%)	Al_2O_3 (%)	Fe_2O_3 (%)	MnO (%)	MgO (%)	CaO (%)	Na_2O (%)	K_2O (%)	P_2O_5 (%)	LOI (%)	Total (%)
Light burned MgO	11.36	0.02	0.57	0.33	0.02	71.67	4.06	0.13	0.13	0.02	11.67	99.98
Dead burned MgO	0.92	<0.01	0.16	0.34	<0.01	96.80	1.33	0.01	<0.01	<0.01	-	99.99
Silica Fume	88.18	<0.01	0.62	1.39	0.14	3.28	0.93	0.85	2.67	0.22	1.66	99.92

Samples preparation and testing methods

Paste and mortar samples of MgO and silica fume were prepared using a Hobart mixer. A MgO/SiO_2 ratio of 50/50 by mass (equivalent to Mg/Si molar ratio of 1.5) was selected which should result in the formation of both brucite and M-S-H as hydration products. The w/c (water to cement) ratio was 0.4 while the sand to cement ratio was 1 for the mortar samples. 3% superplasticizer, by mass of binder, was added to improve the workability. In terms of the magnesium phosphate cement, the ratio of magnesium to phosphate was 4:1 with a w/c ratio of 0.18.

The hydration temperatures during early ages were monitored by temperature sensor under insulated conditions. The setting time was measure as per the standard ASTM C191 - 13. Compressive strength tests were performed at 7, 28, and 90 days, according to ASTM C 109-02. The mortar samples were cast in 50×50×50 mm cube moulds and demoulded after 24 h before curing in water at 20°C. SEM analysis was performed on hydrated paste samples at 28 days using a JEOL 6400 Scanning Electron Microscope. The development of hydration products was monitored at 1, 7, 28, 90 days using a Philips PW1729 X-ray diffractometer (Cu, 50 kV/40 mA) with a 3 to 70° 2θ scan range.

The fresh pastes were placed in sealed polystyrene tubes and stored in an environmental chamber at the temperature of 21°C until testing date.

RESULTS AND DISCUSSION

Hydration temperature of magnesium phosphate cement

The early age heat generated during the hydration of MPC is shown in Figure 2. It can be seen, the temperature increased rapidly in the first thirty minutes after it was mixed with water. This indicates that the hydration reaction between the magnesium oxide and the water soluble phosphate occurred very quickly. After the heat evolution reached the peak of approximately 38 ^{o}C it quickly decreased which indicates a significant reduction in the hydration reactions.

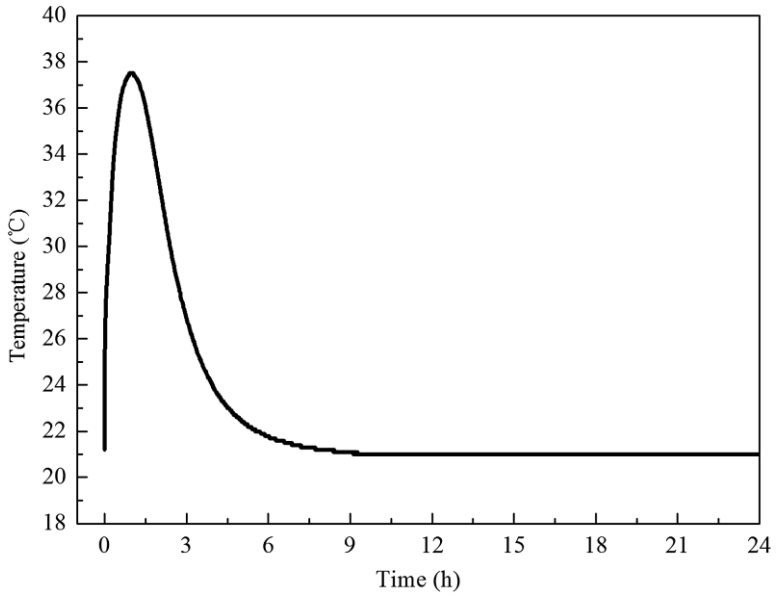


Figure 2. The hydration temperature profile during the early age of MPC samples.

Fresh properties of magnesium phosphate cement

The two fresh properties of setting time and the fluidity were examined. The relatively short setting times of the MPC are considered an advantage due to its application as a repair material. If the MPC sets to quickly however there is insufficient time for placing and handling the material and borax can be added as a retarder which increases the setting time to approximately 18mins to allow for mixing and casting. It should be noted that for MPC, unlike the Portland cement (PC), the period between the initial and final setting time is extremely short thus it's very hard to differential initial and final setting.

The fluidity of MPC was measured at 163mm in diameter when using the flow table test as per IS: 1199 – 1959. The fluidity of the PC is generally better than that of MPC if just comparing the diameter of the sample. The w/c ratio of 0.18 for MPC however was much lower than the w/c ratio of 0.5 for PC.

The fluidity of the MPC can be improved by adding supplementary cementitious materials as shown in Figure 3. With the incorporation of fly ash or slag, the fluidity of the sample noticeably increased as typically occurs in more conventional PC systems. While the addition of fly ash or slag was shown to increase the fluidity of the MPC they resulted in a decrease in the setting time.

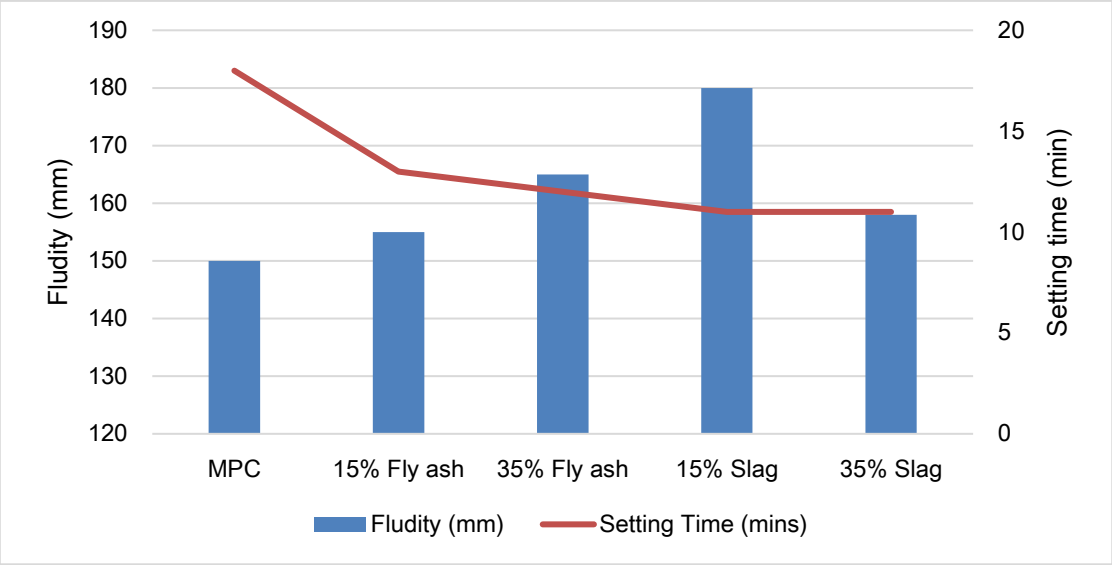


Figure 3. The workability of MPC with different content of fly ash and slag

Compressive strength

The MPC specimens showed very high early age strength achieving 55 MPa after only one day. By comparison a General Purpose (GP) Portland cement with a w/c ratio of 0.4 for instance would be expected to achieve a 7 day strength of approximately 40 MPa. The main factors that affect the strength are water to cement ratio, phosphate to magnesia ratio, fineness of magnesia and the curing conditions. In Fig.4, MPC samples are compared with MSH samples. Over the first 90 days it can be seen that the strength of the two magnesium binder systems developed in very different ways. The MPC achieved a strength of 61 MPa after only 7 days but showed very little additional strength gain and in fact a slight reduction was noted after 90 days. The strength of the MSH mortar continued to increase over the study period from 25 MPa at 7 days to 54 MPa at 90 days. It is likely the MSH samples will continue to gain strength beyond 90 days but further testing is necessary. The moderately high 28 and 90 day compressive strengths of the MSH mortars of 40 and 54 MPa respectively, indicating this material is potentially suitable for many structural applications.

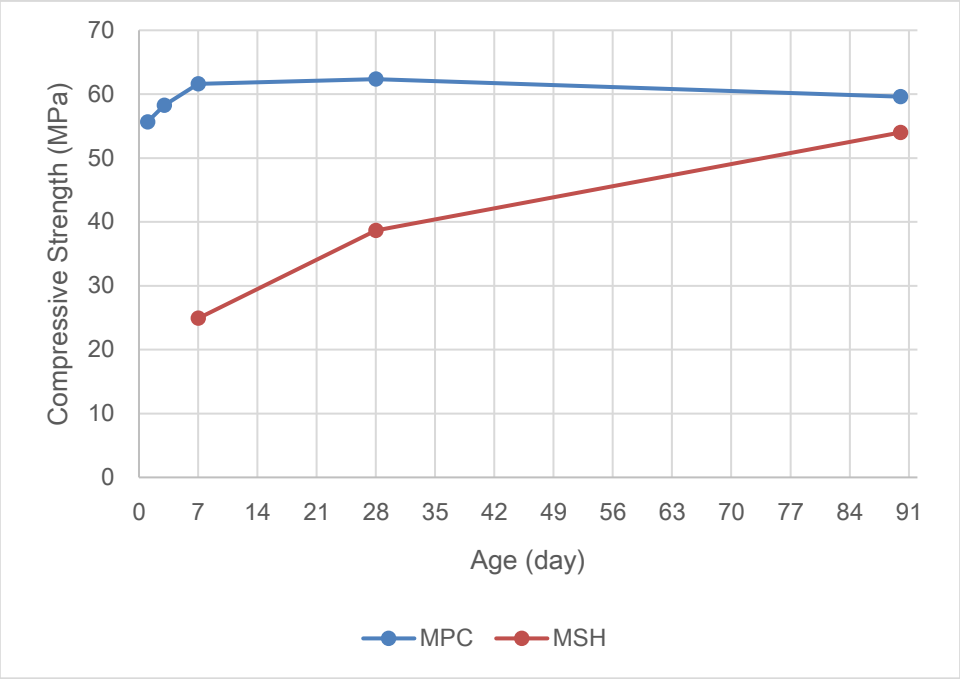


Figure 4. Strength development of MPC and MSH samples

Figure 5 shows the compressive strength development of MPC samples under different curing conditions. The sample under controlled curing condition, defined as 24 °C and 90% humidity in Table 4, showed the highest strength after 28 days. High temperature curing was shown to increase the early age (3 days) strength. While the application of elevated curing temperatures accelerated the reaction rate it lead to the production of poor crystallized hydrates with very little additional strength gain. The 28 day strength was essentially unchanged from the 3 day value.

The reaction of magnesium with phosphate can release a large amount of heat, allowing MPC to still react even under fairly low temperatures but with relative low hydration rate and strength development.

The specimens that were cured in water demonstrated that MPC system is not stable when in contact with water as was evident by then significant decrease in compressive strength compared to the controlled curing samples. The poor water stability is the main weakness of the MPC as it limited the application of the new binder. The poor stability is believed to be caused by the water soluble property of the phosphate. The unreacted phosphate can dissolve into water resulting in an increase in porosity of the samples and a drop of the strength.

Table 4. Strength of MPC under different curing conditions.

	Temperature / ℃	Humidity / %	Compressive strength /MPa			
			1d	3d	7d	28d
Controlled curing	24	90	47.7	53.6	67.8	69.8
High temperature	40	90	43.9	58.2	59.4	60.5
Low temperature	2	90	42.8	46.0	46.6	49.3
Water curing	24	100	44.8	33.0	29.6	22.7

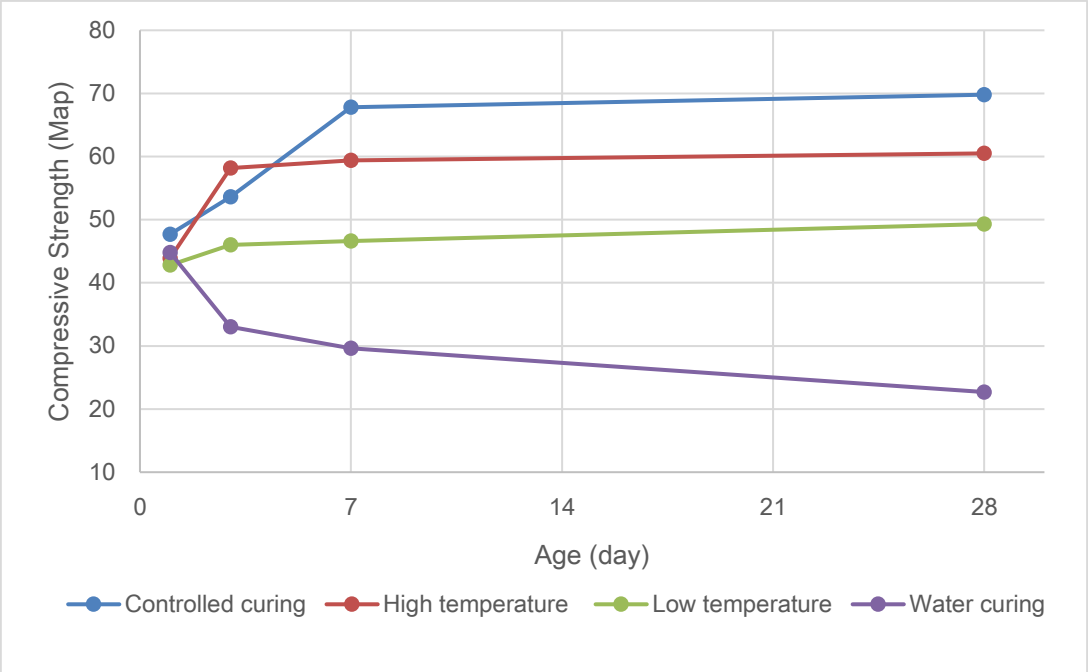


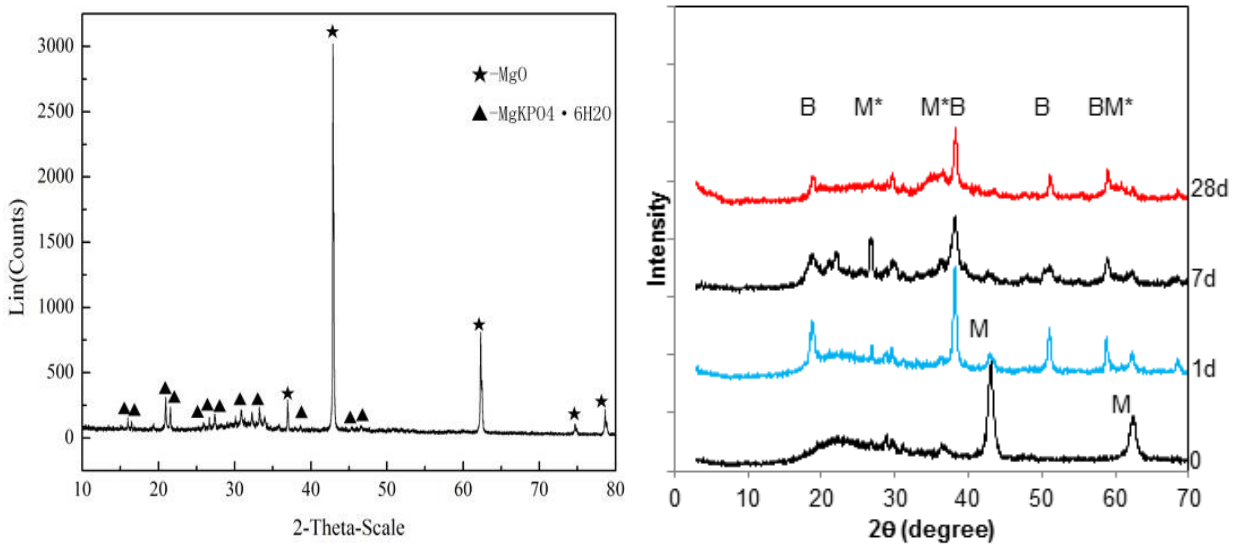
Figure 5. The compressive strength of MPC sample under different curing conditions

XRD analysis

Fig. 6 presents XRD patterns of MPC and MSH paste samples up to 28days of curing. Mixtures of the raw materials before mixing with water were denoted by age 0 while hydration development was analysed at 1, 7, and 28 for the MSH samples. It can be seen from Fig.6(a), the magnesium is abundant in the material even after 28 days and the main hydration product is $MgKPO_4 \cdot 6H_2O$. The main reaction for MPC is summarized as follow:

$$MgO + KH_2PO_4 + 5H_2O = MgKPO_4 \cdot 6H_2O \qquad \text{equation (1)}$$

It was found that curing duration had a significant effect on the type of hydration products of M-S-H binders. Fig. 6b shows XRD spectra of MSH mixtures in which the majority of MgO was consumed in just the first day, illustrated by the reduction in intensity of MgO peaks compared to the raw mixtures. The formation of a large amount of brucite at this very early age is confirmed by the presence of brucite's peaks at $2\theta^o$ = 18°, 38°, 51°, 59°. This is consistent with what has been observed elsewhere (Vandeperre 2008; Jin and Al-Tabbaa 2013). The hydration of MgO was almost completed after 7 days, as the MgO's peaks disappeared at this age. However, the observed amount of brucite at 7 days decreased as part of the freshly formed brucite subsequently reacted with silica fume to form M-S-H phases. According to previous studies (Gollop and Taylor 1992; Temuujin 1998a, b) three major broad peaks at 20–30°, 32–39°, and 58–62° 2θ have been assigned to MSH gels. At 28 days age, these broad XRD peaks are clearly visible, which indicates the formation of poorly crystalline layered magnesium silicate hydrate phases as a result of the reaction between brucite and silica fume. It can be seen that some residual brucite was still present at 28 days.

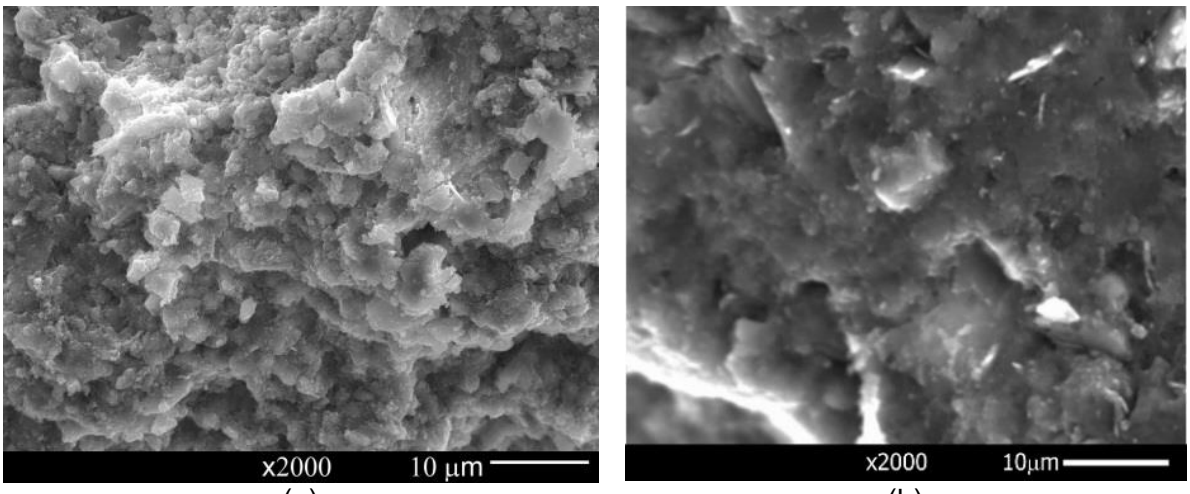


(a) (b)

Figure 6. XRD spectra of: a) MPC paste at 28 days, b) MSH paste samples (M: MgO, B: Brucite, M*: M-S-H, Q: quartz)

SEM analysis

A control sample of 100% reactive MgO (w/c=0.40) cured for 28 days was prepared to compare microstructure of brucite with MSH samples. The relatively porous microstructure of 100% brucite sample is shown in Figure 7a while the microstructure of MgO-SF mixtures with MgO/SiO_2 ratio of 50/50 at 28 days is provided in Figure 7b. MSH gel was observed by SEM analysis at 7 days (not shown) despite no clear indication from the XRD spectra. The brucite content was high at 7 days age however reduced considerably at 28 and 90 days. The 28 day SEM image is consistent with a reduction it the amount of brucite and increase in the MSH phases.



(a) (b)

Figure 7. 28 day SEM image of a) brucite, b) magnesium silicate hydrate

In Figure 8, the microstructure of MPC can be seen and the energy dispersive spectroscopy analysis identified the elements of the crystals. In accordance with the XRD result, the main hydration product of the magnesium phosphate cement is the crystal $MgKPO_4 \cdot 6H_2O$.

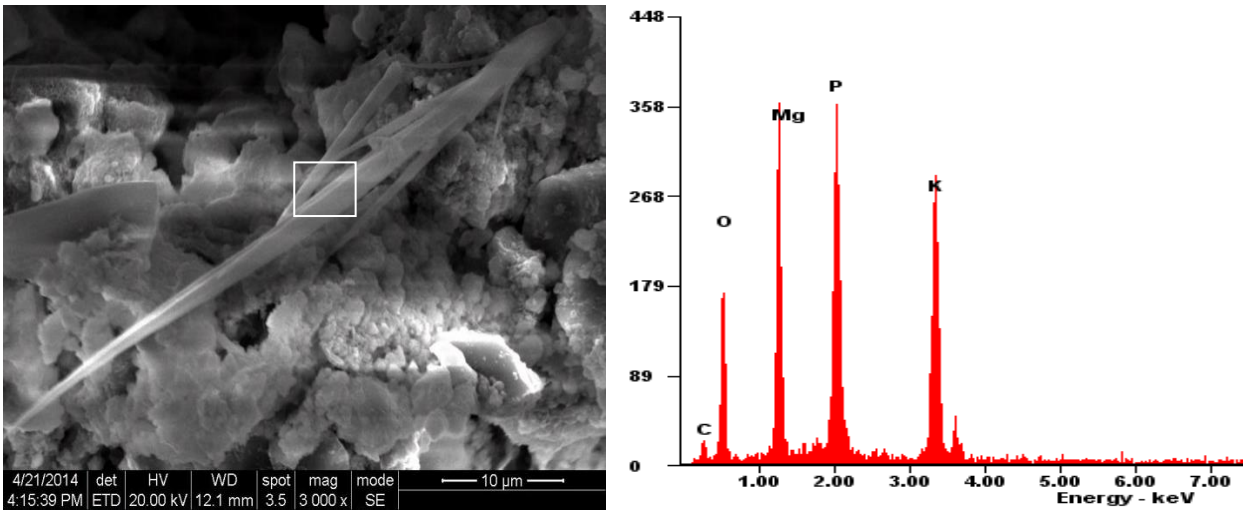


Figure 8. Microstructure and energy dispersive spectroscopy of MPC at 28d

CONCLUSION

Magnesium oxide can be mixed with both silica fume and soluble phosphate (mono-potassium phosphate in this case) to form cementitious materials. The reaction between magnesium oxide and phosphate is very quick and releases a large amount of heat. As a consequence, it showed a much higher early strength compared to either MSH or ordinary Portland cement. The high early strength is one advantage for application of MPC as a repairing material. However, the strength of MPC began to decrease significantly when in contact with water. Further research is necessary to improve the water resistance of the MPC before it can be used as a general purpose construction or repair material.

Unlike the soluble phosphate, silica fume is very stable in water and is known to react with MgO to form a MSH binding phases. In the present investigation mixtures of reactive MgO and silica fume, at w/c ratio of 0.40 and ambient conditions, resulted in the formation of brucite dominant hydration products after 1 day and 7 days. While MSH was initially observed at 7 days it became the dominant phase at longer curing periods. The MSH system displayed moderately low early compressive strengths but the continued hydration and formation of MSH resulted in 28 and 90 days strengths of 40 and 54 MPa respectively which are potentially suitable for a wide range of structural applications.

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